Last time: 9/21

$$S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r$$

For microcanonical distribution:

$P_r = \frac{1}{\Omega}$ if r is in the allowed region

0 if r is not allowed.

$$S = -k \sum_{\substack{r=1 \\ \text{allowed}}}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k \sum_{r=1}^{\Omega} \frac{1}{\Omega} (-\ln \Omega) =$$

$$= k \frac{\ln \Omega}{\Omega} \overbrace{\sum_{r=1}^{\Omega} 1}^{\Omega} = k \ln \Omega$$

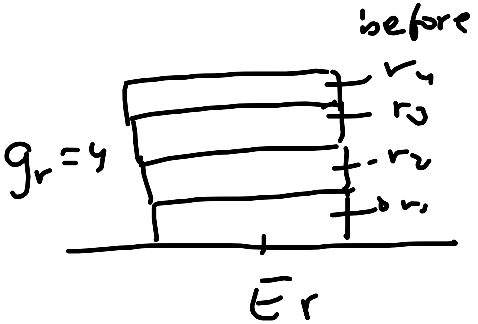
expression of S in microcanonical

Partition function and density of states:

If ϵ_r has degeneracy g_r then

$$Z_N(V,T) = \sum_r g_r e^{-\beta \epsilon_r}$$

now we consider the different values of ϵ_r (while before many of the ϵ_r's may have been identical to each other)



and

$$P_r = \frac{g_r e^{-\beta \epsilon_r}}{\sum_r g_r e^{-\beta \epsilon_r}}$$

For a macroscopic state $\frac{\Delta E}{E} \ll 1$ then E can be considered continuous.

Then $P(E)\,dE$: probability of finding the system with energy in the interval $(E, E+dE)$.

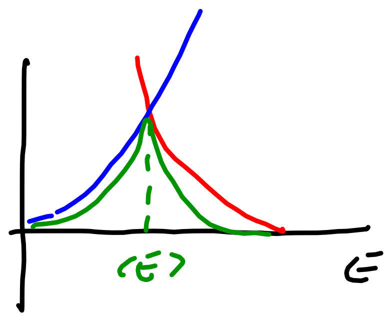
$$P(E)\,dE \propto e^{-\beta E} \underbrace{g(E)}_{\text{density of states.}}\, dE$$

Normalizing $P(E)\,dE$ to 1:

goes to zero with E

increases with E

$$P(E)\,dE = \frac{e^{-\beta E} g(E)\,dE}{\int_0^\infty e^{-\beta E} g(E)\,dE}$$



Now

$$Z_N(V,T) = \int_0^\infty e^{-\beta\epsilon} g(\epsilon)\, d\epsilon$$

Looks like a Laplace's transform.

and

$$\langle f \rangle = \sum_r f_r P_r = \frac{\sum_r f_r(\epsilon_r)\, g_r\, e^{-\beta\epsilon_r}}{\sum_r g_r\, e^{-\beta\epsilon_r}} \rightarrow$$

$$\rightarrow \frac{\int_0^\infty f(\epsilon)\, e^{-\beta\epsilon} g(\epsilon)\, d\epsilon}{\int_0^\infty e^{-\beta\epsilon} g(\epsilon)\, d\epsilon}.$$

Laplace's transform:

$$F(s) = \int_0^\infty e^{-st} f(t)\, dt$$

$t \geq 0$

s is complex

$s = \sigma + i\omega$

$$Z_N(T) = \int_0^\infty e^{-\beta E} g(E)\, dE$$

identifying

$\beta \equiv s$

$E = t$

So $g(E)$ can be obtained if we know Z_N by applying the antiLaplace's transform.

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Z(\beta)\, d\beta \qquad \text{for } \beta' > 0$$

$$g(\epsilon) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{(\beta'+i\beta'')\epsilon} Z(\beta'+i\beta'')\, d\beta''$$

$\beta = \beta' + i\beta''$ integration in complex plain

In practice we are going to use tables of Laplace's transforms.

The canonical ensemble formalism for classical systems:

We will have to work in phase space.

$$\langle f\rangle = \frac{\int f(p,q)\,\rho(p,q)\,d^{3N}q\,d^{3N}p}{\int \rho(p,q)\,\underbrace{d^{3N}q\,d^{3N}p}_{d\omega}}$$

over all phase space

much simpler and without the microcanonical constraints.

We said when we demonstrated Liouville's theorem that $\rho(q,p) \propto e^{-\beta H(q,p)}$ satisfied $[H,\rho]=0$

Liouville's.

$$\therefore \quad \langle f\rangle = \frac{\int f(q,p)\,e^{-\beta H}\,d\omega}{\int e^{-\beta H}\,d\omega} \qquad d\omega = d^{3N}q\,d^{3N}p$$

Then

$$Z_N(V,T) = \frac{1}{N!} \int e^{-\beta H(q,p)} \frac{d\omega}{h^{3N}}$$

# of states in $d\omega$

unit of phase space volume ω_0

to correct the overcounting if the N particles are indistinguishable (Gibb's recipe).

$$Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int_{\text{all phase space}} e^{-\beta H(q,p)} d\omega$$

Ideal gas (classical, N particles, 3D):
V, T (equilibrium).

$$H(p,q) = \sum_{i=1}^{N} \frac{p_i^2}{2m} \qquad p_i^2 = (p_x)_i^2 + (p_y)_i^2 + (p_z)_i^2$$

$$\therefore\ Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int_{\text{all space}} e^{-\frac{\beta}{2m}\sum_{i=1}^{N} p_i^2} \prod_{i=1}^{N} d^3q_i\, d^3p_i =$$

$$\prod_{i=1}^{N} \int_0^L \cdots \int_0^L d^3q_i$$

$$= \frac{V^N}{N!\,h^{3N}} \left[\int e^{-\frac{p^2}{2mkT}} \underbrace{d^3p}_{4\pi p^2\,dp} \right]^N =$$

$$= \frac{V^N}{N!\,h^{3N}} \left[4\pi \int_0^\infty p^2 e^{-\frac{p^2}{2mkT}} dp \right]^N$$

4π — integration over θ and φ

Looking the defined integral on a table:

$$Z_N(V,T) = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m kT)^{3/2}\right]^N \qquad \text{using } \ln N! \simeq N\ln N - N$$

Then:

$$F(N,V,T) = -kT\ln Z_N(V,T) = -kTN\left[\ln\left\{\frac{V}{h^3}(2\pi mkT)^{3/2}\right\} - \ln N + 1\right] = kTN\left\{\ln\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] - 1\right\}$$

It is identical to what we very painfully obtained using the microcanonical formalism.

Now we can obtain:

$$\mu = \frac{\partial F}{\partial N}\Big|_{V,T} \qquad P = -\frac{\partial F}{\partial V}\Big|_{N,T} = \frac{NkT}{V}$$

and

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N}$$ which will be the same as we obtained in microcanonical

How do we obtain the energy of the gas?

$$U = -\frac{\partial \ln Z}{\partial \beta}\Big|_{E_r} = F + TS = \frac{3}{2}NkT$$

$E_r \equiv$ constant volume

$$Z \propto T^{\frac{3N}{2}} \Rightarrow -\frac{\partial \ln Z}{\partial T}\frac{\partial T}{\partial \beta} = \frac{kT^2}{T^{3N/2}}\frac{3N}{2}T^{\frac{3N}{2}-1} = \frac{3kTN}{2}$$

$\partial \beta = -kT^2$

$$\beta = \frac{1}{kT} \quad \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$$

Also:

$$Z_N(V,T) = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi m k T)^{3/2}\right]^N \equiv$$

$$\equiv \frac{\left[Z_1(V,T)\right]^N}{N!} \quad (*)$$

Z_1: single particle function

(*) valid if there are no interactions nor quantum correlations among the particles.

Knowing $Z_N(V,T)$ we can obtain $g(E)$ for the 3D ideal gas:

$$g(\epsilon) = \mathcal{L}^{-1}(Z(\beta))$$

$$Z_N = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$F(\beta) = \beta^{-3N/2}$$

$$f(t) = \mathcal{L}^{-1}(F(s)) \quad \Bigg| \quad F(s) = \mathcal{L}(f(t))$$

$$t^n \quad \Bigg| \quad \frac{n!}{s^{n+1}}$$

$$E^{\frac{3N}{2}-1} \quad \Bigg| \quad \frac{\left(\frac{3N}{2}-1\right)!}{\beta^{\frac{3N}{2}}}$$

$$E = t$$

$$\beta = s$$

Then

$$g(E) = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N (2\pi m)^{3N/2} \frac{E^{\frac{3N}{2}-1}}{\left(\frac{3N}{2}-1\right)!}$$

Now that we found $g(\varepsilon)$ you can check that

$$Z_N(V,T) = \int_0^\infty e^{-\beta\varepsilon} g(\varepsilon)\, d\varepsilon = \frac{1}{N!}\left(\frac{V}{h^3}\right)^N \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

Also in 9/12 class we found that for 1 particle in a 3D box:

$$a(\varepsilon) \approx \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2}$$ single particle

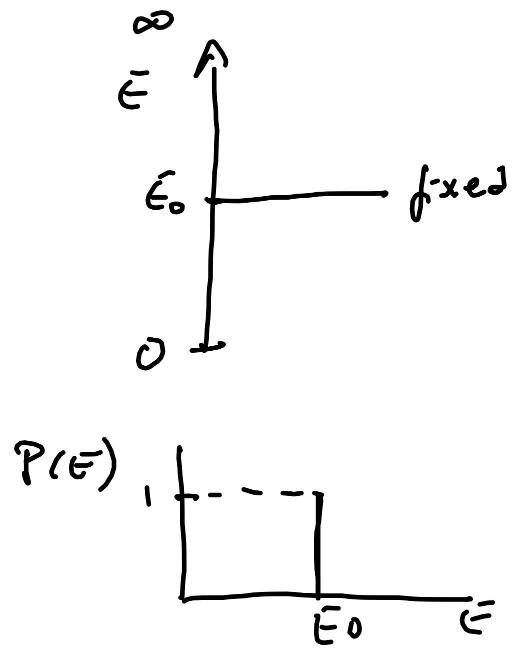
then

$$Z_1(V,T) = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$ and $$Z_N = \frac{Z_1^N}{N!}.$$

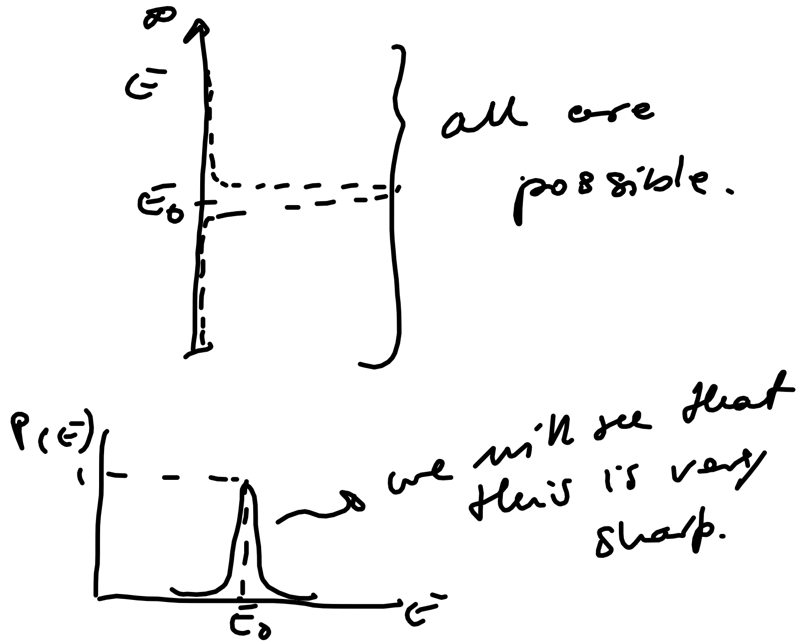
Energy fluctuations in the canonical ensemble:

Equivalence between canonical and microcanonical:

Microcanonical



Canonical



In canonical:

$$U = \langle \epsilon \rangle = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\langle (\Delta\epsilon)^2 \rangle = \langle (\epsilon - \langle \epsilon \rangle)^2 \rangle = \langle \epsilon^2 - 2\epsilon\langle\epsilon\rangle + \langle\epsilon\rangle^2 \rangle$$

$$= \langle \epsilon^2 \rangle - 2\langle\epsilon\rangle^2 + \langle\epsilon\rangle^2 = \langle\epsilon^2\rangle - \langle\epsilon\rangle^2 \overset{D/}{=}$$

$$= -\frac{\partial U}{\partial \beta}$$

$$\langle \epsilon^2 \rangle = \frac{\sum_r \epsilon_r^2 e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$$

D/

$$\frac{\partial U}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}\right] = -\frac{\sum_r \epsilon_r^2 e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} + \frac{\left(\sum_r e^{-\beta \epsilon_r} \epsilon_r\right)^2}{\left(\sum_r e^{-\beta \epsilon_r}\right)^2}$$

$$\langle(\Delta E)^2\rangle = -\frac{\partial U}{\partial \beta} = -\frac{\partial U}{\partial T}\frac{\partial T}{\partial \beta} = \frac{1}{k\beta^2}\frac{\partial U}{\partial T} =$$

$$= \frac{(kT)^2}{k} c_V = kT^2 c_V$$

Then the relative root-mean-square fluctuation is:

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E\rangle} = \frac{\sqrt{kT^2 \overbrace{c_V}^{\sim N}}}{\underbrace{U}_{\sim N}} \propto \frac{1}{\sqrt{N}} \xrightarrow[N\to\infty]{} 0$$

$\therefore$ then the distribution is very sharp -

we will see that it looks like a very sharp gaussian, almost like a δ.